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It is shown that ISFETs are closely related to conventional ion selective electrodes. The time response characteristics of these devices are examined in detail. The possibility of their use as direct charge sensors is critically evaluated.

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ELECTROCHEMISTRY OF CHEMICALLY SENSITIVE FIELD EFFECT TRANSISTORS

by

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ELECTROCHEMISTRY OF CHEMICALLY SENSITIVE FIELD EFFECT TRANSISTORS

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Introduction

The addition of ion sensitive field effect transistors (ISFET) to the
family of chemical transducers over a decade ago [1,2] has opened new
possibilities for both applied and fundamental electroanalytical
investigations. Later, first transistors sensitive to electrically neutral
species, hydrogen, has been reported [3] and a new acronym CHEMFET (chemically
sensitive field effect transistor) has been introduced in order to accommodate
this type of sensor. The development of this new class of sensors is by no
means complete. Field effect transistor is primarily a charge measuring device
and a preamplifier which has low and well defined input capacitance, high
input impedance and can be made very small. For this reason new types of
physical, electrochemical and biomedical measurements are possible with this
device. In this paper I shall try to point out a few electrochemical aspects
of ISFETs.

Ion selective electrode (ISE) is the closest relative of ISFET. It is
customary to discuss their performance in isolation. With ISFETs it is
necessary to consider the whole measuring system including the solid state
part of the device, the reference electrode and even the connections between
these components. From this point of view we need to discuss two groups of
devices: once in which the ion sensitive membrane is part of a symmetrical
arrangement (i.e., solution/membrane/solution) and those with the arrangement,
solution/membrane/solid contact. Conventional ISE with internal filling
solution/reference electrode fall ito the first category while coated wire

electrodes, hybrid devices and ISFETs fall into the second. The potential

profiles in these two structures are shown in Figure 1. The equivalent

electrical circuit of the membrane shown in Figure 1a (symmetrical case) is in

Figure 2. If this membrane is ion selective it is always possible to design

the composition of the solutions in such a way that the interfacial

resistances R_1 and R_2 are small. The value of the bulk resistance R_b is

usually dictated by the composition and geometry of the membrane. Although it

is of secondary importance it is advantageous to keep R_b at the minimum. In

terms of electrode kinetics the interfacial charge transfer resistance (R_{CT} =

R_1, R_2) is related to the exchange current density (i_o) at the interface by the

relationship

$$R_{CT} = \frac{RT}{nFi_o} \tag{1}$$

in which R, T, n and F have their usual meaning. The partial ionic currents

due to all charged species which can cross the interface contribute to i_o. If

one species alone carries most of the current relative to the others the

membrane is said to be selective to that particular ion. If, at the same time

the absolute magnitude of this current is high ($> 10^{-5}$ A cm^{-2}) the electrode

is pragmatically labelled as "good" because it is not affected by motion of

the electrolyte or adsorption. Conversely, if i_o is equally high but there is

no dominating single ionic species responsible, the interface is non-selective

and for all purposes behaves as a liquid junction. On the other hand, if the

exchange current density is low ($\leq 10^{-9}$ A cm^{-2}) it follows from Eq. 1 that the interface at which the analytical signal is generated is essentially a high (output) impedance source. As an ion selective membrane such device would earn a label "bad" because it would "drift" respond to adsorption of ion-ionic species and to motion of the electrolyte.

Clearly, the exchange current density is one of the most important parameters which determines the behavior of ion selective membranes. This fact has been recognized [4] and a semiquantitation interpretation of the response of "bad" ion selective electrodes and certain ISFETs has been given [5,6]. Ironically, a close coupling of the "bad" membrane to the preamplifier can seemingly "improve" the situation.

The equivalent circuit in Figure 3 describes the asymmetrical devices (Figure 1b). The reference electrode, liquid junction, and the sample solution of Figure 1b are lumped together as E_{REF}. The section "SOLID" can be a conductor, such as in coated wire electrodes, hybrid sensors or ISFETs with thin metallic coating or it can be an insulator such as in other ISFETs. The "VOLTMETER" can be an electrometer (for coated wire electrodes) or an integrated circuit (for a hybrid) or the solid state portion of the ISFET. The two interfaces (impedances) in question are one and two. Let us first assume that the exchange current density at the interface one is high (a "good" ISE). If i_o at interface two is also high the inner electrical potential of the solid contact is uniquely determined by the equality of the electrochemical potential (i.e., Fermi level) of the exchanging charged species in the bulk of the membrane and in the bulk of the conductor. As long as the leakage resistance (shown in the circle) is higher then the lowest of R_1, R_2 or R_b the

potential profile throughout this structure will be stable. Several coated wire electrodes and hybrids fit this description, the example being [7]: solution $F^-/LaF_3/AgF/Ag/Cu$.

Let us now consider the case that the charge transfer resistance R_2 is very high, so much so that this interface becomes capacitive. In that case the parasitic capacitance (shown in Figure 3 in circle) must be small and invariable and the parasitic resistance must be infinitely high in order to obtain a stable output from the volumeter. It is obvious that the shorter the solid conductor the better are these conditions satisfied. In other words, if the interface between the membrane and the solid is capacitive the problems increase with the length of the lead. An ISFET in which the membrane is placed directly at the input insulator of the voltmeter is an extreme case in which the length of the conductor is zero. The corollary of this statement is that there is no difference in principle between all the sensors discussed above. In practice, however, the differences can be substantial.

Finally, we need to consider the case of a "bad" membrane, that is the one which has low exchange current density at interface one, that is this interface is a leaking capacitance. In a fixed geometry arrangement, such as in an ISFET or a hybrid with short lead a deceptively stable and reproducible signal can be obtained [6]. Such a device is, however, nearly non-selective and all the problems discussed above will be added to the complications which are caused by the interface two. In short, it is not possible to make a good sensor out of a bad membrane.

Time Response of ISFETs

In the equivalent circuit in Figure 3 the capacitors C_1, C_b, C_2 and the input capacitor of the voltmeter are in series whereas the parasitic capacitor (in circle) is in parallel. If this latter capacitor is very small the system

will respond to a rapid change of applied potential as a capacitor divider, that is - instantaneously. The simplified formula for the time response of the gate-to-source voltage, V_{GS}, of an ISFET is [8,9]

$$V_{GS}(t) = V_o(1 - \frac{C_{GS}}{C + C_{GS}}) \exp[-t/R(C + C_{GS})] \qquad (2)$$

where V_o is the applied voltage step, C_{GS} is the input capacitance, and R and C are the lumped parallel resistance and capacitance of the membrane, respectively. It follows from the Equation (2), that if $C > 0.1 C_{GS}$, such as commonly happens in ISFETs, a finite voltage $V_{GS}(t=0)$ appears across V_{GS} at time was and the time response to electrical step of the gate voltage becomes

$$V_{GS}(t=0) = V \frac{C}{C + C_{GS}} \qquad (3)$$

as is shown in Figure 4. In practice, however, the time response to a concentration step is always limited by the diffusion of the species to the surface of the electrode (Warburg impedance) and only the exponential response is seen. For polymeric membrane ISFETs this time constant is typically in milliseconds [10,11] and for micro ISFETs it is in hundreds of milliseconds [12].

Determination of Exchange Current Density

It follows from the previous qualitative discussion that the exchange current density at each interface of any ion selective sensor is of paramount importance. This parameter can be obtained from complex plane analysis of impedance of electrical equivalent circuits of these devices as has been used by Buck [3] and others for analysis of ISEs response. We have adopted so-

called equilibrium noise analysis [8] which is perhaps more sensitive to values of partial impedances shown in Figure 3.

The instantaneous value of the drain current $I_D(t)$ can be expressed as

$$I_D(t) = \bar{I}_D + i(t) \qquad (4)$$

where $\bar{I}_D$ is the mean value of the drain current and $i(t)$ is its random fluctuation (noise). There are several ways by which $i(t)$ can be studied. We have originally adopted [8] a so called spectral density analysis [14] and we are currently investigating the correlation analysis [15]. The latter technique enables us to distiguish between the device noise and the electrochemical noise. The procedure for spectral analysis is as follows: the time record of the equilibrium ISFET noise is converted into the frequency domain using the Fourier transformation yielding so called power spectrum. At this point we again use the equivalent circuit approach but now we separate the noise sourses $V_1 - V_3$ (Figure 5a) from "noiseless" resistors $R_1 - R_3$. The partial power spectra and the overall theoretical spectrum corresponding to this situation are shown in Figure 5b. The shape, the magnitude and the position on the frequency axis are very sensitive to the values of C's and R's. It is then necessary to match the calculated spectrum with experimental one (Figure 6). If the impedances in Figure 5a represent 1 – the solution/membrane interface; 2 – the bulk; and 3 – the membrane/insulator interface the values of the corresponding exchange current densities can be calculated from Eq. 1. We have followed this

procedure for K^+ ISFET, Na^+ ISFET, and pH ISFET. In the first two devices the exchange current densities at the solution/membrane interface were found to be in the range of "good" membranes although the exact estimate could not be made because of the uncertainty of the surface area. The electrochemical noise generated by the pH ISFET was obscured by the device noise and for this reason the cross-correlation technique [15] is now being used.

Direct Measurement of Interfacial Charge

Let us assume that the interface one in Figure 3 is ideally polarized, i.e., capacitive ($R_1 = \infty$). Provided that the parasitic capacitance is small, the excess charge at this interface can be measured directly [16], in principle. We have explored this possibility using a CHEMFET with a thin layer of gold deposited over the gate. Gold/sodium fluoride solution is a good approximation of a polarized interface which is described by the Gibbs-Lippmann equation

$$d\gamma = q^m \, dE^{\pm} + \sum_i \Gamma_i \, d\mu_i \tag{5}$$

where γ is the surface energy, q^m is charge on the metal, $E^{\pm}$ is the interfacial potential, Γ_i is so called surface excess of adsorbed ions and μ_i is the chemical potential of adsorbing species. The change of the interfacial potential with activity of adsorbing ion in solution a_i at constant charge on the metal, so called Esin-Markov coefficient, can be derived from Eq. 5:

$$\left(\frac{\partial E^{\pm}}{\partial \ln a_i}\right)_{q^m} = -RT \left(\frac{\partial \Gamma_i}{\partial q^m}\right)_{a_i} \tag{6}$$

The condition of constant metal charge can be easily achieved by using the feedback circuit shown in Figure 7. It is known that iodide ion adsorbs strongly at the gold interface yielding value of the Esin-Markov coefficient of 59 mV/decade. In our initial experiments [17] we could obtain only a transient response of the interfacial potential to the addition of iodide which indicated that the charge transfer resistance at the gold interface had a finite value. The origin of this problem has been traced to the presence of residual oxygen in solution, to the presence of titanium in the surface of the gold and to the surface conductivity of the surrounding silicon nitride [18]. The first problem has been circumvented by thorough deareation of the solution followed by cathodic prepolarization of the gold. The presence of variable amounts of titanium in thin films of gold could not be eliminated, however. Titanium is used as an underlay in order to improve adhesion of gold to silicon nitride. It has been found that Ti diffuses along the grain boundaries [19] over a few thousand angstroms in a few days even at room temperature. When it reaches the metal/solution interface it substantially reduces the charge transfer resistance.

We found the third problem, the surface conductivity of method silicon nitride, totally surprising. In the study of that problem we have taken the advantage of the dual CHEMFET configuration of our transistor chip. By charging up one of the gold gates in air we could observe the effect (cross talk) of migrating charge on the other gate which was left on purpose electrically floating. When the devices were placed in dry nitrogen, essentially no cross talk has been observed over the period of 24 hours. Under

those conditions the surface resistivity has been estimated to be 4×10^{18} ohms/square. Similar results has been obtained for devices covered with a thick layer of cured Epon 826 epoxy even so when encapsulated devices were immersed in water for several hours. However, even a brief exposure of bare silicon nitride to humidity decreased this value. Fully hydrated silicon hydrated silicon nitride was found to have surface resistivity of 1.3×10^{16} ohms/square which dissipated the deposited charge with time constant of 20-30 minutes.

For the direct measurement of Esin-Markov coefficient both the surface contamination with titanium and the surface conductivity of silicon nitride have been overcome by attaching a short piece ($\sim$ 2 mm) of gold wire to the gate and then totally encapsulating the whole chip. With this arrangement we have determined the Esin-Markov coefficient of the adsorption of iodide on gold to be 53.6 mV/decade.

The Gibbs-Lippmann equation (Eq. 5) is the equation of state. In that case the following relationship holds for the state variables:

$$\left(\frac{\partial E^{\pm}}{\partial \mu_i}\right)_{q^m} \left(\frac{\partial \mu_i}{\partial q^m}\right)_{E^{\pm}} \left(\frac{\partial q^m}{\partial E^{\pm}}\right)_{\mu_i} = -1 \tag{7}$$

It will be noted that the first term is the Esin-Markov coefficient (Eq. 6) and the third term is the differential capacitance C_d. Provided that the above partial differentials are smooth, continuous, and non-singular functions of μ_i the second term can be obtained experimentally from its inverse [20]. The relationship between this parameter and the Esin-Markov coefficient is then

$$\left(\frac{\partial E^{\pm}}{\partial \ln a_i}\right)_{q^m} = \frac{1}{C_d} \left(\frac{\partial q^m}{\partial \ln a_i}\right)_{E^{\pm}} \tag{8}$$

Experimentally this means that we have substituted the measurement of interfacial potential at constant charge for measurement of interfacial charge at constant potential. The experimental arrangement for this measurement is shown in Figure 8. In this circuit the potential applied to the reference electrode is V_r while the transitor gate is connected to the feedback voltage V_f through a 10^8 Ω resistor. The potential difference $V_f - V_r$ is then the constant interfacial potential $E^{\pm}$ in Eq. 7. If an adsorbing anion is added to the interface the induced negative charge is compensated by the feedback circuit in order to maintain the set value of the drain current. The signal is, therefore, the transient current flowing through the 10^8 resistor which then integrated yields the supplied amount of charge. By this technique we have estimated the slope of the dependence of adsorbed iodide on solution concentration to be 2.9×10^{-6} C cm^{-2} mole^{-1} l. The Eq. 7 automatically offers a self-consistency check of these measurements with C_d measured independently to be 50×10^{-6} F cm^{-2} the product of the three terms is -0.93 which is in good agreement with theoretical value of -1.0.

Conclusions

Undoubtedly, the interest in CHEMFETs is largely due to their potential as a miniature multisensor with excellent signal-to-noise ratio. Their relationship to other potentiometric sensors is relatively straightforward: the underlaying principles are the same the differences are mainly practical. Because CHEMFETs as well as other potentiometric sensors with solid internal contact are multilayer structures, it is important that the exchange current

densities at the boundaries of these layers are as high as possible. In other words, it is preferable that these surfaces are ohmic.

The preliminary results show that CHEMFETs can be used for basic electrochemical studies, such as investigations of the stochastic events at interfaces and for measurement of interfacial charge. Our experience with these devices also shows that most problems are related to the choice of materials, namely to the encapsultion.

Acknowledgements

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Figure Legends

Figure 1. Potential profile through: (A) symmetrical ion selective electrode (B) non-symmetrical ion selective device.

Figure 2. Equivalent electrical circuit of the ion selective membrane in symmetrical arrangement.

Figure 3. Equivalent electrical circuit of a nonsymmetrical ion selective device.

Figure 4. Computer simulation of the time response of an ISFET with different geometry. (Reprinted from Ref. 8, with permission).

Figure 5. Electrical equivalent circuit (A) and calculated noise spectra for an ISFET. (Reprinted with permission from Ref. 8).

Figure 6. Noise spectra of ■: Na^+ ISFET; ●: K^+ ISFET O: pH ISFET. The continuous lines correspond to the computer model. (Reprinted with permission from Ref. 8).

Figure 7. Circuit for direct measurement of the Esin-Markov coefficient. (Reprinted with permission from Ref. 17).

Figure 8. Circuit for the measurement of the Esin-Markov coefficient by indirect method. (Reprinted with permission from Ref. 18).

A   CONVENTIONAL ISE
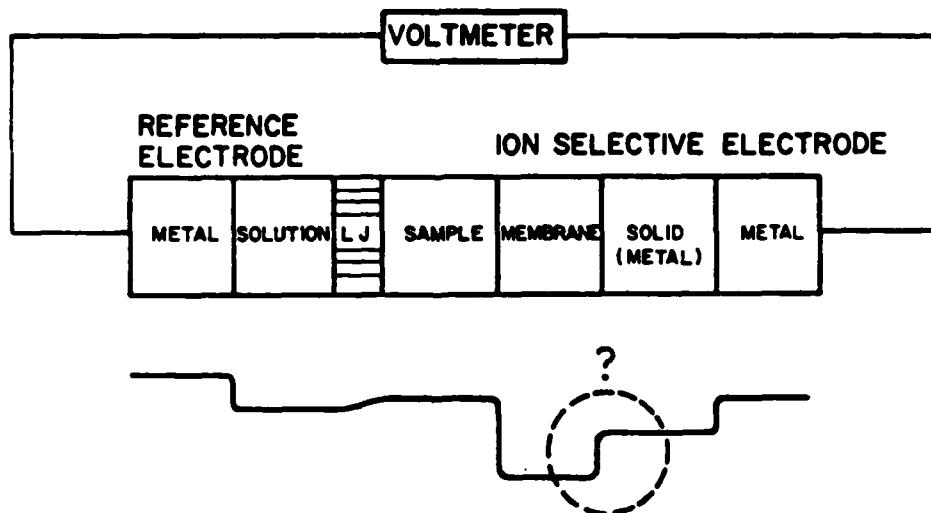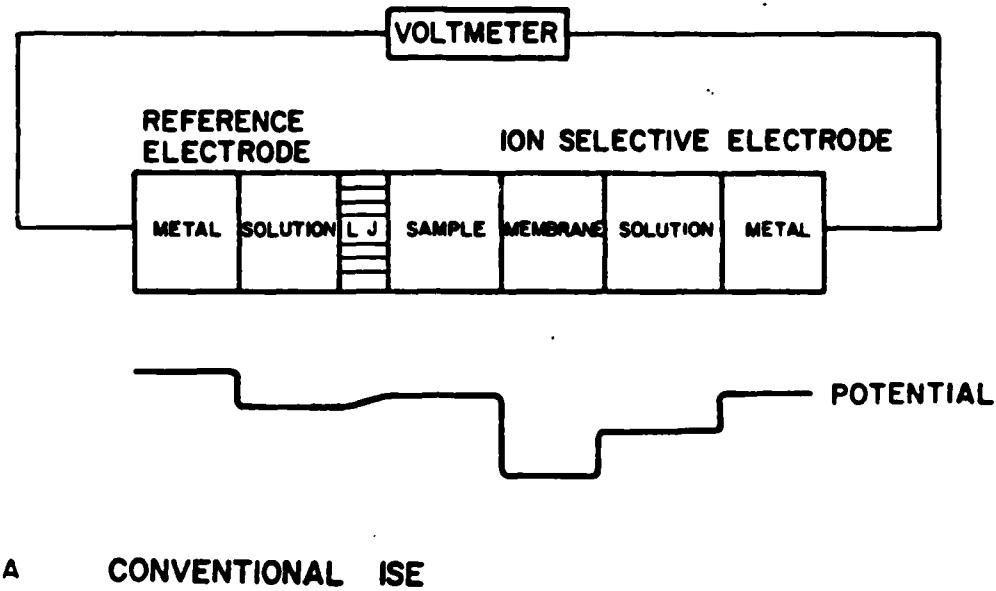
B   COATED WIRE ELECTRODES

     HYBRID SENSORS

     ISFETS

Figure 1.
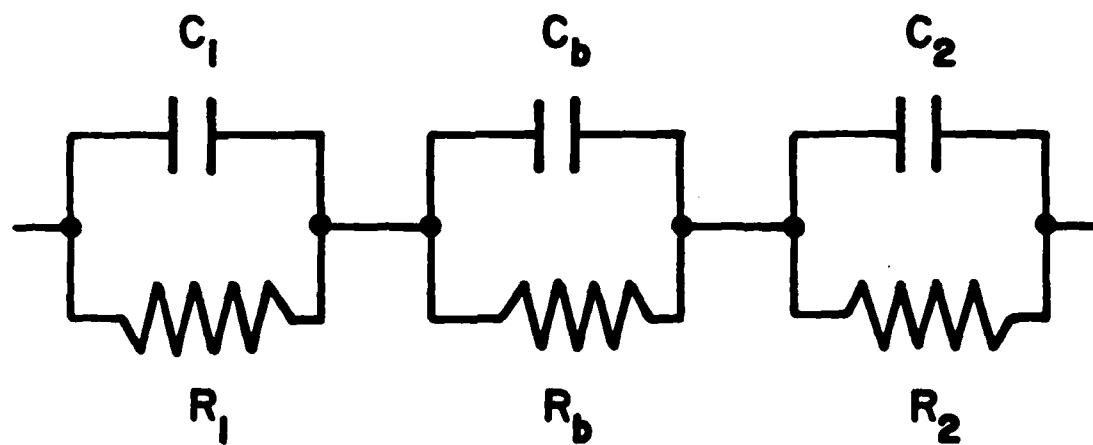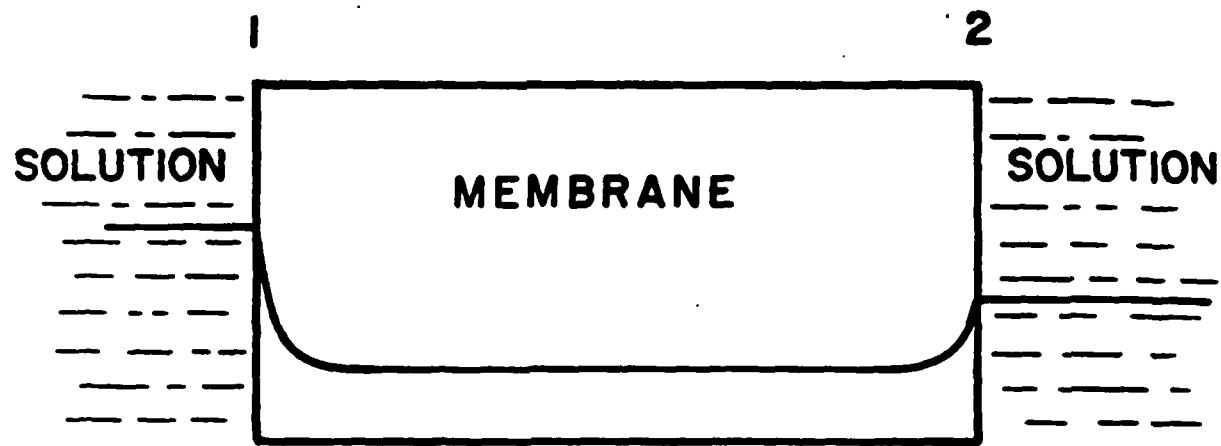
FOR A D.C. RESPONSE

$$R = R_1 + R_b + R_2$$

Figure 2.
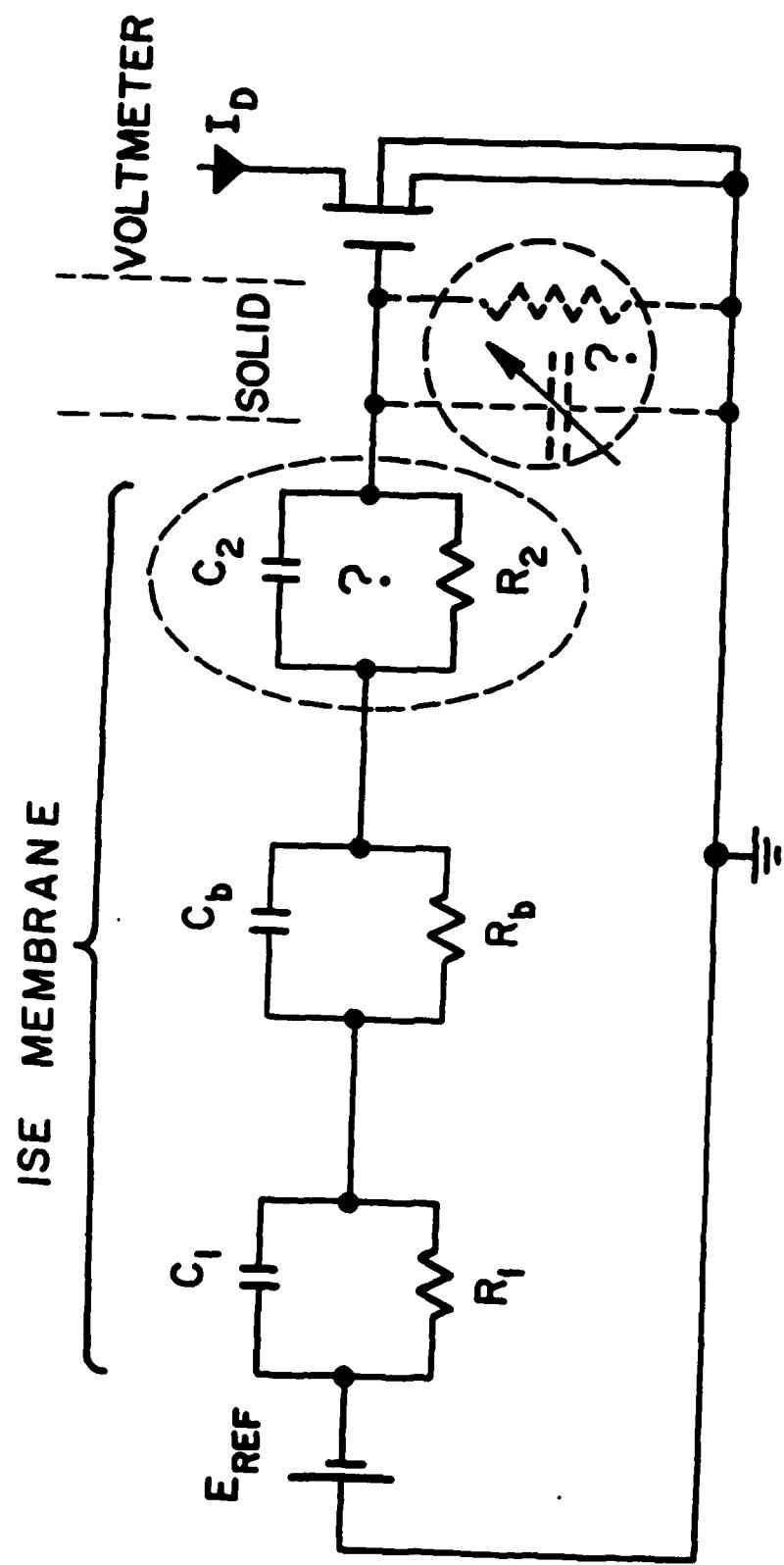
Figure 3.

a

b

Figure 4.

NOISE MODELING
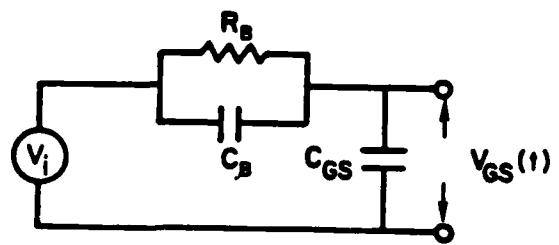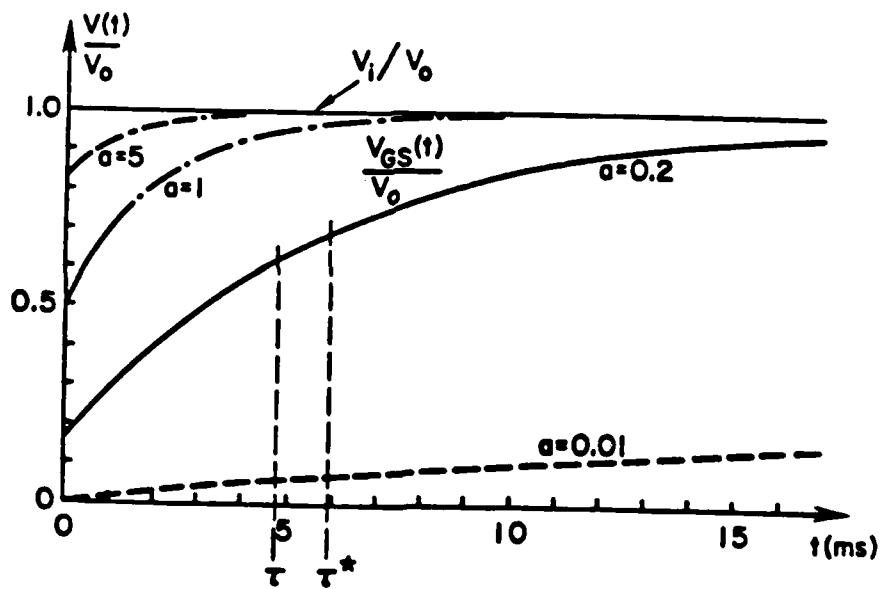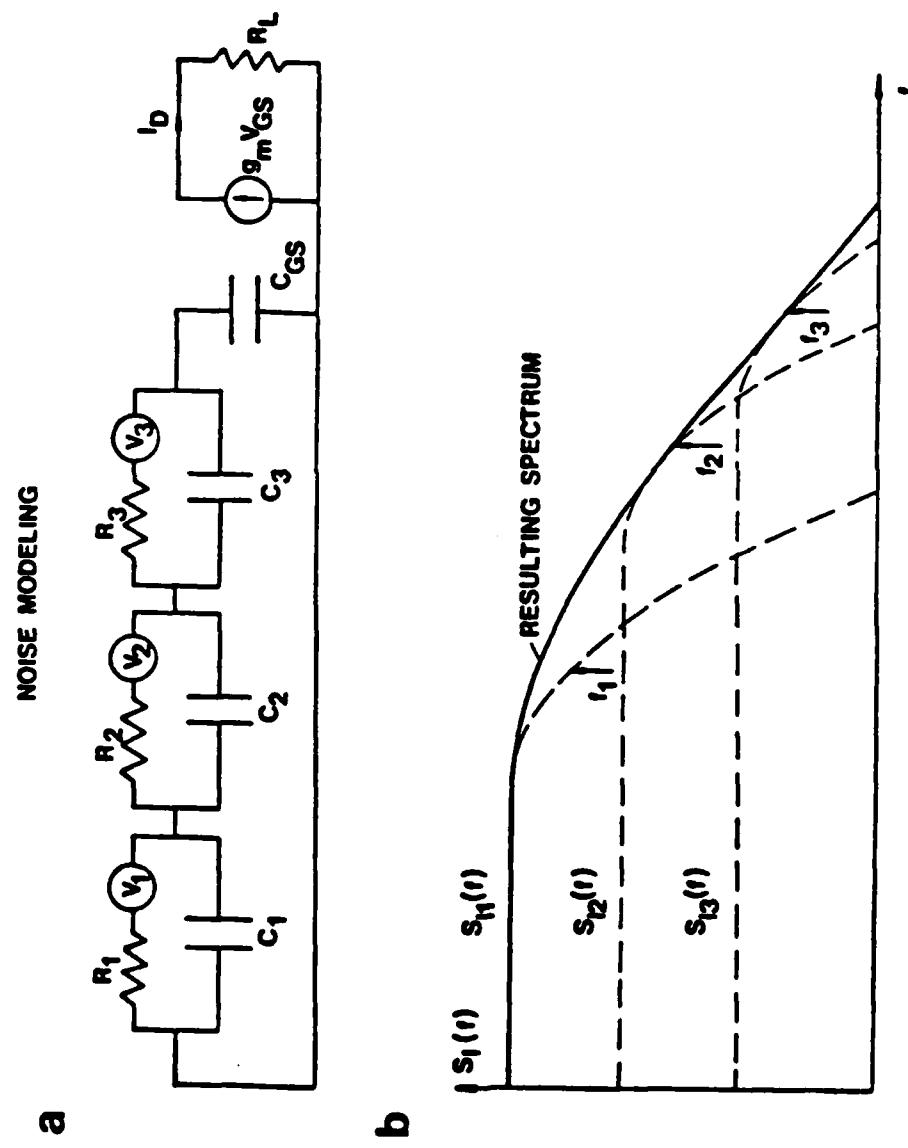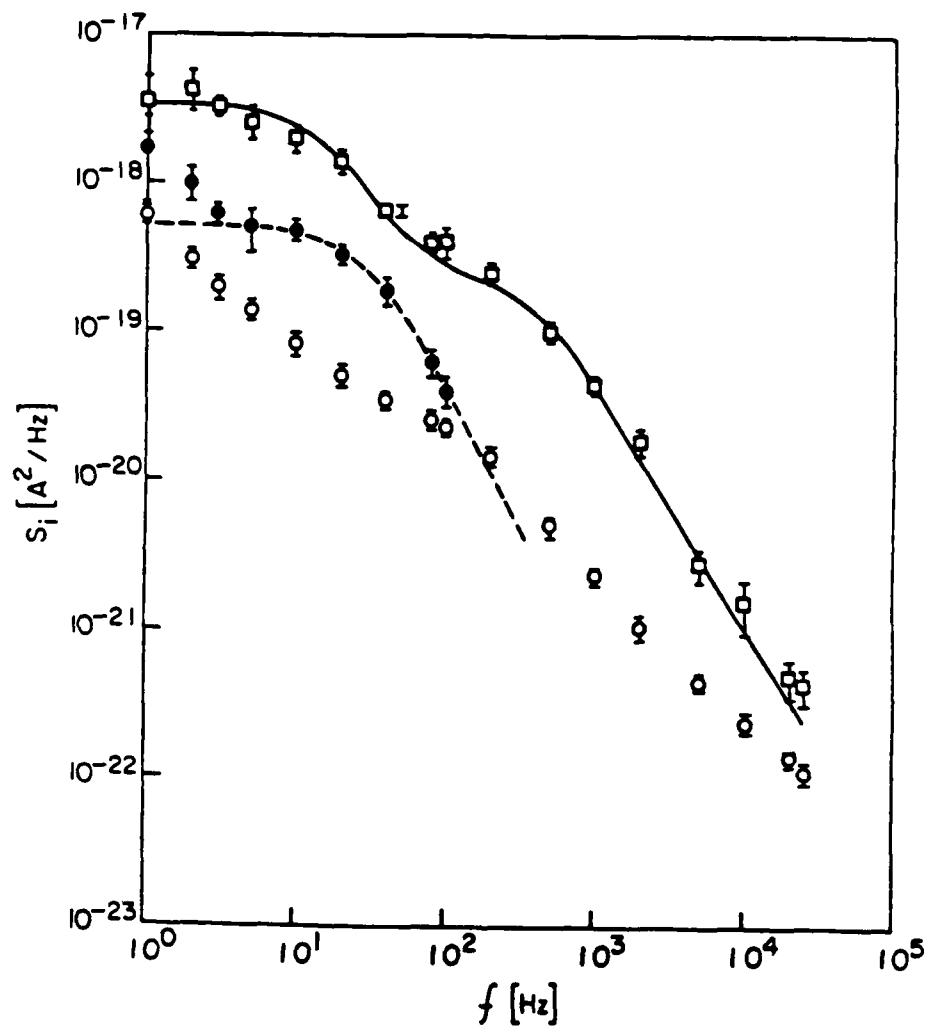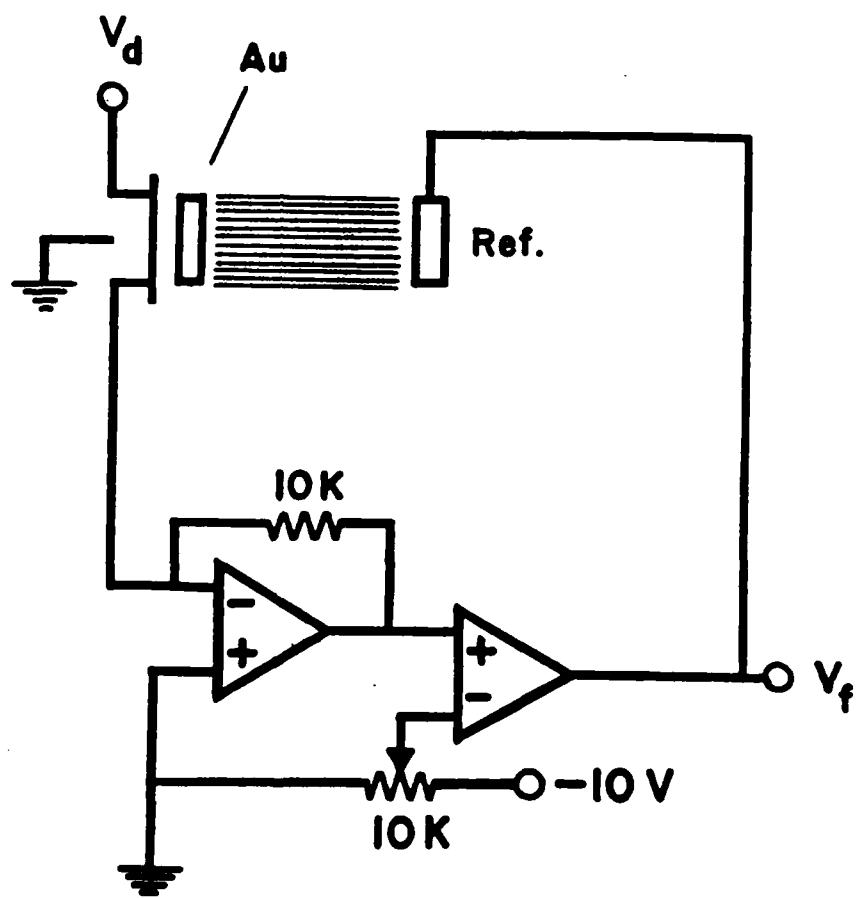
Figure 5.

Figure 6.

Figure 7.
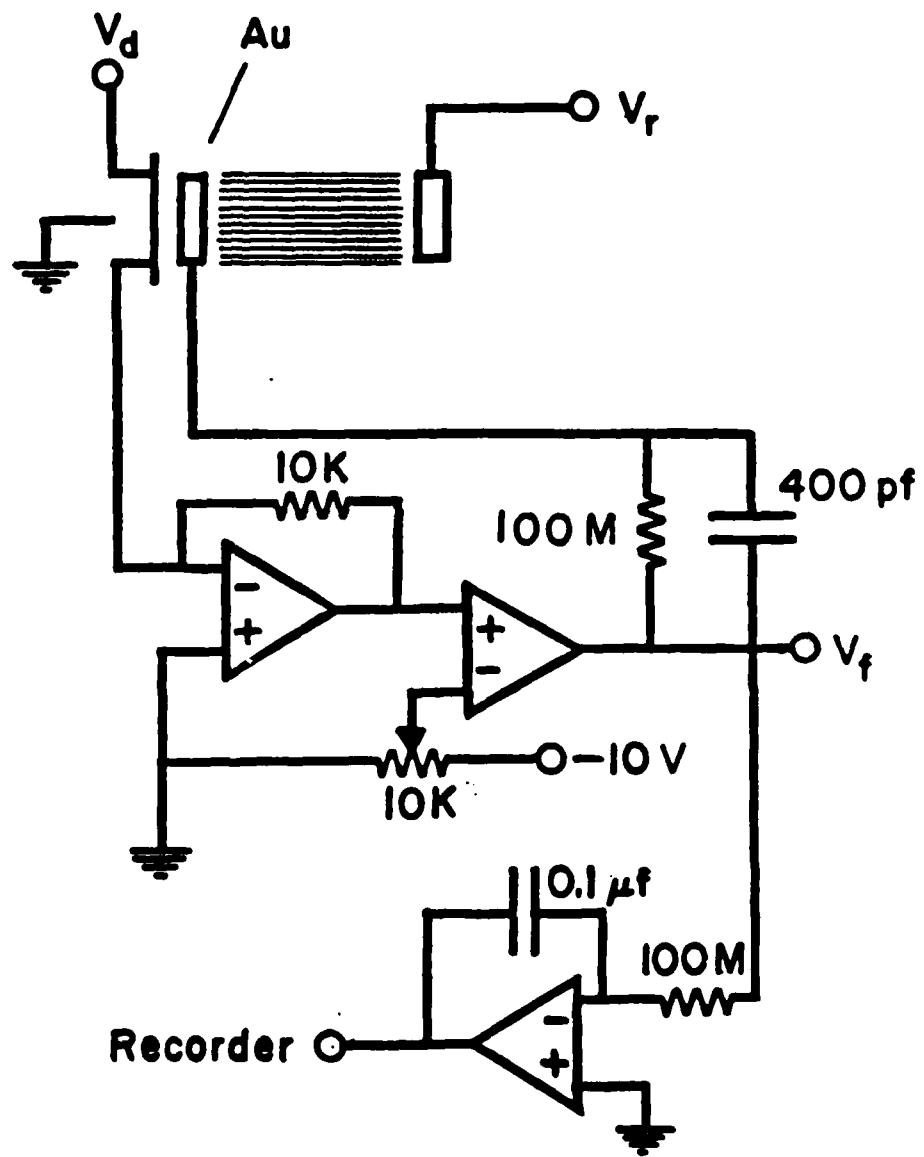
Figure 8.

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